

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

NO DRAWINGS

Thermosettable Coating Formulations and Coated Articles

WE, THE DOW CHEMICAL COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of Midland, County of 5 Midland, State of Michigan, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly 10 described in and by the following statement:—

This invention relates to new coating and laminating formulations containing a combination of certain thermo plastic film-forming addition polymers and epoxides. 15 The invention also includes the articles coated with the compositions and laminates prepared with the compositions.

Thermoset coatings and laminates based 20 on the concept of a thermoplastic material crosslinked with an epoxide are known in the prior art. These coatings or laminates when cured are infusible and solvent insoluble and accordingly are admirably 25 adapted for the coating of metallic substrata, such as home appliances, office furniture, and similar articles. It is traditional for these materials to be deposited from compositions employing an organic 30 solvent as the vehicle. Typical of the epoxides used in the prior compositions are the condensation products of epichlorohydrin with diphenylolpropane. Although such materials are operable in the aforementioned crosslinking function, nevertheless certain problems arise particularly in the solubility characteristics of the epoxy resin and in the resulting film properties 35 such as resistance to the deleterious effects of ultra-violet light. 40

This invention provides new coating and laminating formulations which are cross-linkable with certain epoxides to produce

coatings and laminates which have high solvent resistance and good resistance to the effects of ultra-violet light.

The coating or laminating formulations of this invention comprise (1) an organic solvent and (2) dissolved therein film-forming solids composed essentially of a 50 film-forming addition polymer containing a relatively high proportion, i.e., 5 to 20 weight percent, of an α,β -unsaturated carboxylic acid interpolymerized with another monomer and a glycidyl ether of an 55 aliphatic polyol or an epoxy novolac having at least two oxirane rings per molecule. The formulation preferably contains from 50 to 95 percent by weight of said solids of a film-forming addition polymer composed of 60 from 7 to 12 percent by weight of the α , β -unsaturated carboxylic acid interpolymerized with from 93 to 88 percent by weight of at least one ethylenically unsaturated comonomer, from 50 to 5 65 percent by weight of said solids of the polyepoxide and a catalyst for accelerating the crosslinking reaction. The invention further includes the coated or laminated articles comprising the substratum and the 70 insoluble, infusible coating or laminating adhesive.

The addition polymeric component of the composition is a thermoplastic resinous material derived from 5 to 20 percent preferably 7 to 12% by weight of an α , 75 β -unsaturated carboxylic acid. Such polymerizable acids are well known in the art and include typically the monofunctional acids such as acrylic acid, methacrylic 80 acid, ethacrylic acid, and itaconic acid, as well as the dicarboxylic acids, such as maleic acid and fumaric acid, and the polyfunctional acids, such as sorbic acid. Thus, any carboxylic acid which is capable of 85 addition polymerization is operable in the

present invention. The remainder of the polymeric molecule is derived from one or a combination of alkenyl aromatic monomers preferably having from 6 to 10 carbon atoms in the aryl nucleus.

It is well known in the art that changes in the monomeric ratios will alter the flexibility, hardness, and other physical properties of articles made from the polymers prepared therefrom. A preferred thermoplastic resinous material finding utility within the present invention is the copolymer of 85 percent by weight of styrene and 15 percent by weight of methacrylic acid. Although the interpolymer may be of any molecular weight, it is preferred that the molecular weight be relatively low. This permits the preparation of compositions of high solids content which gives greater film thickness per coating.

The epoxide used in this invention is a glycidyl ether of an aliphatic polyol having at least two terminal epoxide groups per molecule and substantially free from reactive substituents other than epoxide and hydroxyl groups. These epoxides include 1, 2-epoxy-containing polyethers of polyhydric alcohols, such as the diglycidyl ether of ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol, diethylene glycol, triethylene glycol and dipropylene glycol. Also included within the scope of the invention are the polyglycidyl ethers of polyhydric alcohols having a 1, 2-epoxy equivalency greater than one, such as the polyglycidyl ethers of glycerol, diglycerol, erythritol, penta-glycerol, penta-erythritol, mannitol, sorbitol, polyallyl alcohol and polyvinyl alcohol. Mixtures and blends of these polyepoxides are also useful in the present inventive concept.

The epoxy novolac which may be employed in the present invention is the condensation product of an epoxylating agent including, for example, epihalohydrin, polyhalohydrin, or polyepoxides with a novolac resin resulting from the condensation of a phenol with an aldehyde. These novolac resins are well-known substances, many of which are available as commercial products. As is known in the art, they are produced by condensing the phenol with an aldehyde in the presence of an acid catalyst with use of a mol ratio of the phenol to aldehyde greater than about 1.1 and up to about 2.5 or about 0.4 to 0.9 mol of aldehyde per mol of the phenol. The phenol to be used in preparing the novolac resin may be mono- or polyhydric so long as there are at least two sites (ortho or para hydroxy activated) open on the aryl ring for condensation with the aldehyde. Thus phenol, resorcinol, alkyl substituted phenols, and similar compounds may be used. Although novolac resins from formalde-

hyde are generally preferred, those resins resulting from the use of other aldehydes, such as, for example, acetaldehyde, chloral, butyraldehyde, furfural can also be used.

In preparing the epoxy novolac resin the condensation is effected by mixing the novolac resin with an amount of epoxidizing agent in excess of the phenolic hydroxyl equivalent of the novolac resin and with addition of alkali metal hydroxide in an amount equivalent to the phenolic hydroxyl equivalent of the novolac. The reaction mixture is maintained at elevated temperature of 60 to 150° C. during the ensuing reaction. Upon completion of the reaction, the formed alkali metal salt and any unreacted hydroxide are removed from the resulting epoxy resin as are also unreacted epoxidizing agent in water. It is essential to the operation of the present invention that each epoxy novolac resin be characterized by having at least two oxirane rings per molecule of epoxy novolac.

The solute of the formulation is composed of from 50 to 95 percent by weight of the film-forming thermoplastic material and from 50 to 5 percent by weight of the glycidyl ether of an aliphatic polyol. The ratio or proportion of each component may be varied rather widely within the stated range to provide optimum physical and chemical coating properties. As a general rule, the ratio of components should be adjusted to provide approximately one epoxide group for each carboxyl group in the polymer. Within the stated range of proportions of the compositions there result thermosettable coatings which following curing or thermosetting exhibit excellent hardness, flexibility, adhesion to various substrata, and water resistance including resistance to boiling water.

For practical reasons it is greatly desired to include in the formulation a catalyst for accelerating the crosslinking reaction between the film-forming thermoplastic resinous material and the epoxide. These catalysts also permit the use of lower temperatures in curing than those required when no catalyst is employed. Typical catalysts finding utility herein are the quaternary ammonium compounds, such as dodecyltrimethylammonium chloride, tetramethyl ammonium chloride, trimethylbenzylammonium acetate and tertiaryamines. When used the catalyst may be present in an amount of up to about 3 percent by weight of the composition.

The formulations may also contain plasticizers, pigments, dyes, reinforcing agents and like materials commonly used in formulating polymeric compositions.

The organic solvents that may be used include, for example, esters, ketones, and mixtures of hydrocarbons with esters and/or

ketones. The particular solvent to be used will depend to great extent in the choice of components selected for the film-forming solids and secondarily in individual preference and economic considerations.

The solids content of the solution will depend on the solubilizing efficiency of the organic solvent for the particular solute chosen and on the desired thickness of the coating. As a general rule of thumb the solute should be present in an amount of from 5 to 60 percent by weight of the total composition.

The formulations of this invention may be used to coat a wide variety of substrata including the common structural metals such as iron, steel and aluminium both primed and unprimed. Thus the formulations are useful for coating automobile parts, home appliances, aluminium siding, cans and the like. The formulations may also be used for coating cellulosic substrata including wood, composition boards, such as particle board and chip board, as well as coating and impregnating paper. The formulations may be employed for saturating fiberglass cloth and similar articles and in preparing a wide variety of laminates.

The procedural sequence whereby the desired products are realized comprises the deposition of the formulation as described above on the substratum followed by volatilization of the solvent and finally by curing the deposit at an elevated temperature.

The coating may be deposited by known coatings techniques useful for lacquers and similar coatings compositions. These include brushing and doctoring with known means.

The solvent may be volatilized by evaporation under normal ambient conditions or by use of slightly elevated temperatures with or without the concurrent application of reduced pressure. The solvent should be substantially completely removed prior to the completion of the crosslinking reaction. When possible it is preferred to volatilize the solvent simultaneously with curing by the elevated temperatures used for the curing step.

The temperature and time schedules to be used in curing the coating to a thermoset adherent film will vary with the components of the composition and the efficiency of the catalyst if one is employed. These temperatures include those which are commonly used for baking protective and decorative coatings. Thus, the metal coating art commonly employs baking temperatures of from 93.3° C. to 260° C. or higher for times of from less than one minute to at least 30 minutes. These baking conditions have been found to cause satisfactory curing of the present coatings. It

will be apparent that the nature of the substratum will also dictate the maximum temperature employed. It will be understood that time and temperature of baking or cure are in inverse relationships to one another so that an increased temperature requires a shorter time to achieve a given state of cure than is required by a relatively lower temperature. To achieve maximum properties it is essential that curing be substantially complete. A substantially complete cure is readily discernible by the infusibility and insolubility and other properties of the resulting product.

The thermoset coatings and laminates of this invention are characterized by good adhesion, initial color and color retention on oven baking or exposure to ultraviolet light, gloss, excellent resistance to acetone, xylene, and similar solvents, and to water and aqueous detergent solutions. They also exhibit good impact resistance, hardness and flexibility, and show resistance to staining from mustard, lipstick, ink, and other household materials.

The advantages and benefits of the present invention will be more apparent from the following illustrative examples wherein all parts and percentages are by weight.

Example 1

One hundred parts of a linear copolymer polymerized from 85 percent styrene and 15 percent methacrylic acid was dissolved in methyl ethyl ketone. To that solution was added 34.3 parts of the diglycidyl ether of dipropylene glycol (epoxide equivalent weight of 197) and 0.5 part of dodecyltrimethylammonium chloride. The solution was doctoring onto a clean unprimed metal panel to a thickness of 0.0025 cm. The coated panel was baked 30 minutes at 177° C. The resultant continuous coating exhibited adhesion to the panel, hardness, flexibility, and other properties necessary for a protective coating for metals.

Example 2

A composition similar to that of Example 1 was prepared using 25.5 percent of the diglycidyl ether of dipropylene glycol and 74.5 percent of the copolymer of that example. This composition is identified below as Composition A.

A similar composition identified below as Composition B was prepared using 26.8 percent of diglycidyl ether of polyepichlorohydrin (epoxide equivalent weight of 210). For comparative purposes another composition identified below as Composition C was made using 27.7 percent of an epoxidized soybean oil (epoxide equivalent weight of 220) sold commercially as Epoxol 7-4 by Swift and Company (Epoxol 7-4 is a registered trade mark). Each of the epoxides used in Compositions B and C replaced the diglycidyl ether of dipropylene

glycol of Composition A. In addition, each composition was formulated to have one epoxide group per carboxyl group.

- Each of the compositions was coated as one mil films onto a polished phosphated steel panel and baked for 30 minutes at 177° C. Each of the panels was tested according to standard procedures with the results listed in the table below. In the mandrel flex test the panel was bent around first a mandrel of 1.27 cm. diameter, then if passed, a 0.63 cm. diameter mandrel, and if no failure is seen with the 0.63 mandrel then finally about a 0.32 cm. diameter mandrel. The result is listed as the mandrel diameter at which failure of the coating occurred or the successful flex around the 0.32 cm. mandrel. Impact resistance was compared by dropping a ball of standard weight at increasing distances and recording the number of inch-pounds of force

required to cause first noticeable failure of the coating. In the acetone test the coated panel was wiped 20 times with a saturated tissue and the condition of the coating noted. The ink stain test involved marking the coating with a "Cado" marking pen, drying for 2 hours and cleaning with mineral spirits. The amount of staining was noted. The detergent test was conducted according to ASTM-D-714-56 run for 48 hours. If no blisters, bubbles, or other defects were noted, the result is listed as O.K. When some failure occurred, the result is indicated by a letter for the number of individual defects (e.g. "M" means a medium number of defects) and by a number indicating the average size of the various individual defects. In the numbering system 2 indicates the defects of largest size and 8 indicates the defects of smallest size.

TABLE

	Knoop Hardness	Mandrel Flex	Impact Resistance	Acetone Resistance	Ink Stain	1 percent detergent @ 71° C.
Comp. A	10	Pass 0.32	22	O.K.	O.K.	O.K.
Comp. B	19	Pass 0.32	20	O.K.	O.K.	O.K.
For Comparison Comp. C	17	Fail 1.27	12	Soft	Severe	M-4

Example 3

- Several white enamels were prepared employing the copolymer listed in the above examples with various epoxides. In the first sample, identified as I, there was used the diglycidyl ether of dipropylene glycol. In the second sample, identified as II, there was used polyepichlorohydrin. In the third, identified as III, there was used the reaction product of 3 moles epichlorohydrin with one mole of tris (hydroxypropyl) glycol. In the fourth, identified as IV, there was used the reaction product of 3 moles epichlorohydrin with one mole of glycerine resulting in a mixture of di- and triglycidyl ethers of glycerine. For comparison, in a fifth sample, identified as V, there was used the diglycidyl ether of bisphenol A having an epoxide equivalent weight of 175. Another comparative sample, identified as VI, was a semi-solid higher homolog of V having an epoxide equivalent weight of 257. Each of the compositions was properly formulated to have one epoxide group for each carboxylic group. The white enamels were prepared using titanium dioxide as pigment in a pigment/binder ratio of one part pigment to one part total binder. The solvent and catalyst were the same as in Example 1.

Each of the enamels was coated on panels, baked for 30 minutes at 177° C. and exposed in a Fadeometer for 1400 hours to

note resistance to ultraviolet light discoloration. Following exposure, the color change was noted visually. The results indicated that Samples I, II and IV showed a very slight change in color. Sample III exhibited no change. Samples V and VI were each moderately yellow with number VI being the poorest of the series.

Each of the samples was exposed to salt spray by scratching the coating, exposing the scratched coating to 5 percent aqueous salt solution at 35° C. for 270 hours. In corrosion creep Samples I to IV were found to be equal to the bisphenol A Samples V and VI.

Example 4

A formulation was prepared by dissolving in methyl ethyl ketone 76.2 percent of a linear copolymer polymerized from 85 percent styrene and 15 percent methacrylic acid and 23.8 percent of an epoxy novolac of a condensation product of phenol and formaldehyde which has been reacted with epichlorohydrin, the epoxy novolac characterized in having an average functionality of about 3.3 epoxy groups per molecule and an epoxide equivalent weight of 180. The coating composition was coated as a one mil film onto a polished phosphated steel panel and baked 30 minutes 177° C. The panel was tested according to the standard procedures with the results listed in the table below.

TABLE

	Knoop Hardness	Mandrel Flex	Impact Resistance	Acetone Resistance	Ink Stain	1 percent detergent @ 71° C.
5	10	Pass 0.32	22	O.K.	O.K.	O.K.
10	Similar results to those of the above examples are noted when interpolymers containing other carboxylic acids are employed. Thus when the interpolymers contain acrylic acid, itaconic acid, maleic or fumaric acids in place of the methacrylic acid and the polymer crosslinked according to this invention, there result thermoset resins having the physical and chemical properties previously mentioned. Likewise, when the styrene is replaced with other monoalkenyl aromatic monomers including vinyltoluene, alpha-methylstyrene or para-tertiarybutylstyrene, similar results are observed.					
15	In addition similar coating properties are observed when the above noted compositions are applied to wood, paper and other cellulosic substrata and to glass and cured at elevated temperatures.					
20	WHAT WE CLAIM IS:—					
25	1. Coating or laminating formulation intending to be spread on a substratum and heated until thermoset, consisting of or containing a reactive epoxy compound, a film-forming polymer, a catalyst for accelerating the crosslinking of the polymer with epoxy compound, and an organic solvent for the foregoing, wherein the reactive epoxy compound is a glycidyl ether of an aliphatic polyol or is an epoxy novolac having at least two oxirane rings per molecule, and the film-forming polymer is an addition polymer derived from one or a combination of alkenyl aromatic compounds and A,B-unsaturated carboxylic acids, the acid representing from 5 to 20 percent of the weight of the addition polymer.					
30	2. Formulation as claimed in claim 1, wherein the acid represents 7 to 12 percent of the weight of the addition polymer.					
35	3. Formulation as claimed in either of claims 1 or 2, characterized in that from 50 to 95 percent by weight of the polymer are employed with from 50 to 5 percent by weight of the epoxy compound.					
40	4. Formulation as claimed in any one of claims 1, 2 or 3 wherein the acid is a monocarboxylic acid.					
45	5. Formulation as claimed in claim 4, wherein the acid is methacrylic or acrylic acid.					
50	6. Formulation as claimed in any one of claims 1, 2 or 3 wherein the acid is a dicarboxylic acid.					
55	7. Formulation as claimed in claim 6, wherein the acid is maleic acid.					
60	8. Formulation as claimed in any one of claims 1 to 7 wherein the film-forming polymer is an addition polymer of an alkenyl aromatic hydrocarbon and the A,B-unsaturated carboxylic acid.					
65	9. Formulation as claimed in any one of claims 1 to 8 wherein the film-forming polymer is an addition polymer of styrene and the A,B-unsaturated carboxylic acid.					
70	10. Formulation as claimed in claim 9 wherein the film forming-polymer is an addition polymer of 85 weight percent styrene and 15 weight percent methacrylic acid.					
75	11. Formulation as claimed in any one of claims 1 to 10 wherein the catalyst is a quaternary ammonium compound.					
80	12. Formulation as claimed in claim 11, wherein the catalyst is dodecyltrimethylammonium chloride.					
85	13. Formulation as claimed in any one of claims 1 to 12 wherein the ration of the addition polymer to the reactive epoxy compound is such as to provide one epoxy group for each carboxyl group in the addition polymer.					
90	14. Method which comprises applying the formulation according to any one of claims 1 to 11 as a coating to paper or other cellulosic substratum, or to a metal or glass, then causing the solvent to volatilize from the coating, and heating to render the coating thermoset.					
95	15. An article coated with a continuous adherent thermoset coating of the reaction product of a reactive epoxy compound and a film-forming addition polymer, wherein the reactive epoxy compound is a glycidyl ether of aliphatic polyol or is an epoxy novolac having at least two oxirane rings per molecule, and the film-forming polymer is an addition polymer derived from one or a combination of alkenyl aromatic compounds and A,B-unsaturated carboxylic acids, the acid representing from 5 to 20 percent of the weight of the addition polymer.					
100	16. An article in accordance with claim 15 characterized in that the polymer is a copolymer of 85 weight percent styrene and 15 weight per cent methacrylic acid, and the epoxy compound is the diglycidyl ether of dipropylene glycol or the condensation product of phenol and formaldehyde which has been reacted with epichlorohydrin to give an epoxy novolac having an average functionality of 3.3 epoxy groups per molecule.					
105	17. An article as claimed in either of claims 15 or 16 characterized in that it consists of, or contains, metal, cellulosic material, or glass.					
110	18. Coating or laminating formulation					
115						
120						

- intended to be spread on a substratum and heated until thermoset, consisting of -or containing a reactive epoxy compound, a film-forming polymer, a catalyst for accelerating the crosslinking of the polymer with the epoxy compound, and an organic solvent for the foregoing, wherein the reactive epoxy compound is a glycidyl ether of an aliphatic polyol or is an epoxy novolac having at least two oxirane rings per molecule, and the film-forming polymer is an addition polymer derived from one or a combination of alkenyl aromatic compounds and A,B-unsaturated carboxylic acids, the acid representing from 5 to 20 percent of the weight of the addition polymer, substantially as hereinbefore described especially with reference to the foregoing examples.
19. An article coated with a continuous adherent thermoset coating of the reaction product of a reactive epoxy compound and a film-forming addition polymer, wherein the reactive epoxy compound is a glycidyl ether of an aliphatic polyol or is an epoxy novolac having at least two oxirane rings per molecule, and the film-forming polymer is an addition polymer derived from one or a combination of alkenyl aromatic compounds A,B-unsaturated carboxylic acids, the acid representing from 5 to 20 percent of the weight of the addition polymer, substantially as hereinbefore described especially with reference to the foregoing examples.
20. A method of preparing the coating formulation according to claim 1 substantially as hereinbefore described.
- BOULT, WADE & TENNANT,
111 & 112 Hatton Gardens,
London, E.C.1.
Chartered Patent Agents.
Agents for the Applicants.